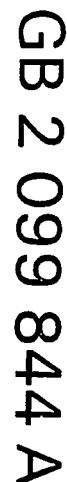
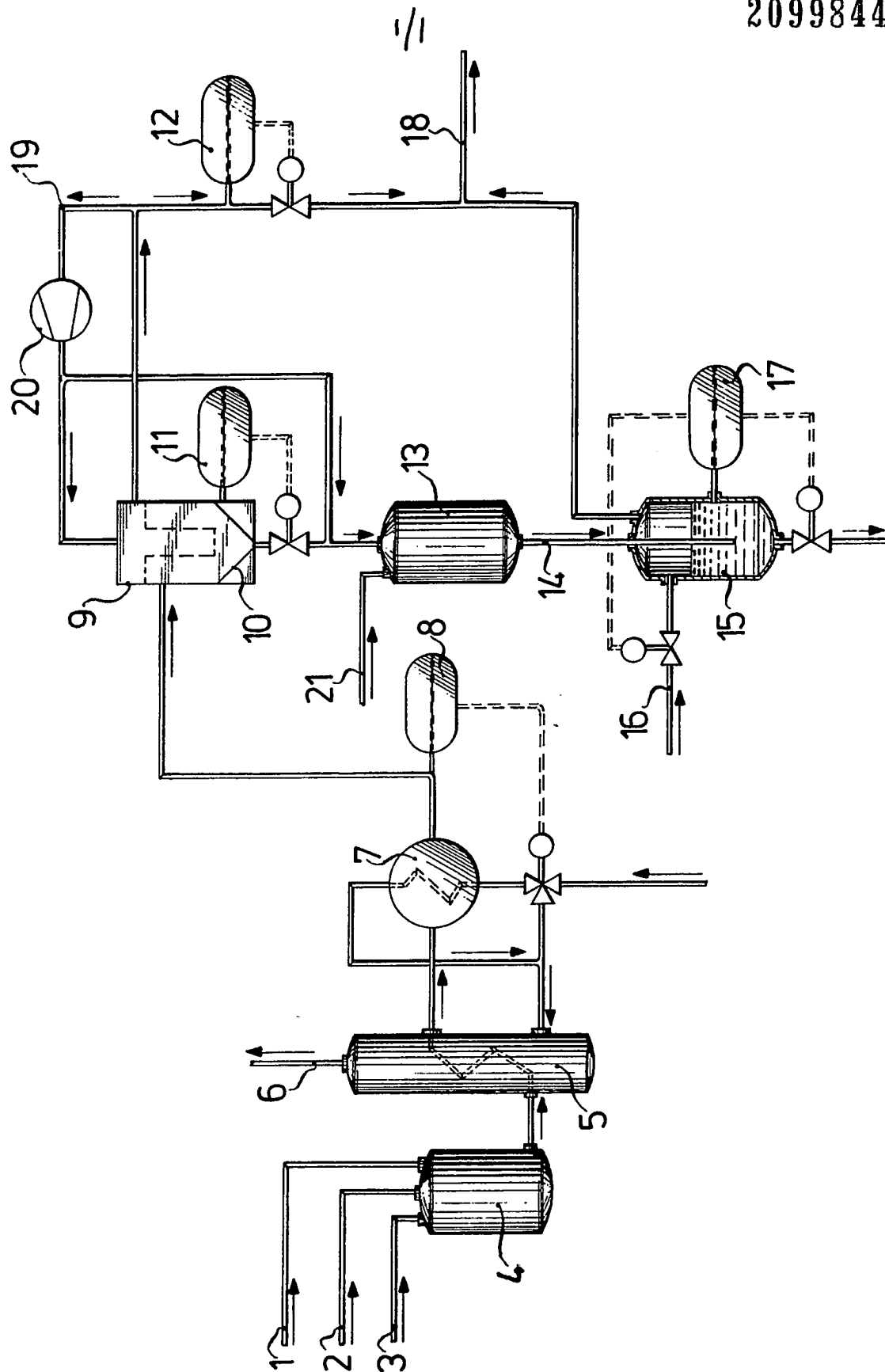


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- (57) **Process for producing synthesis gas**
- (57) One or more hydrocarbons containing nickel and vanadium in a

Preferably no recirculation of the soot to the gasification of the one or more hydrocarbons is effected. The soot may be converted in a reactor, other than one used for the oxidation of the one or more hydrocarbons, into synthesis gas.





SPECIFICATION

Process for producing synthesis gas

The present invention relates to a process for producing synthesis gas from hydrocarbons, especially from ash-rich hydrocarbons.

The conversion of petroleum into synthesis gas, i.e. a mixture of hydrogen and carbon monoxide, may be effected by various processes which differ, *inter alia*, by the nature of the feedstocks, oxidising agents and reaction conditions. Partial combustion of petroleum at elevated pressure has found particularly wide application in synthesis gas production. It is mainly carried out according to two processes developed respectively by Texaco in conjunction with Hydrocarbon Research Inc., and by Shell. In both processes soot is formed as a by-product in an amount of about 1 to 3% by weight referred to the oil feedstock under normal operating conditions, i.e. at 1100 to 1500°C and 10 to 40 bars. The soot is washed out from the gas with water, and is then separated from the water and supplied, usually suspended in oil, as a fuel to the gasification reactor, or is burnt, independently of the gasification process if desired, to produce steam.

Heavy fuel oils such as are used in the Texaco and Shell processes generally contain nickel and vanadium as basic ash constituents. In the gasification process these elements are converted into NiS and V_2O_3 and, disregarding the small amounts remaining in the reactor, are removed with the unpurified gas stream and are separated together with the soot from the gas.

The major proportion of the vanadium/nickel components also is thus found together with the soot. Only a small proportion of the vanadium/nickel components, suspended in water, leaves the process.

The soot may be suspended in oil, such as fuel oil, to facilitate its disposal. In further processing of the soot/oil mixture independently of the gasification process, e.g. by combustion in a power-station boiler to produce steam, even a total level of about 500 ppm of nickel and vanadium do not interfere in the operation of the gasification plant. However, the amount of soot in the oil has to be low, e.g. not greater than 6%, in order to keep the viscosity of the oil at an acceptable value for pumps and burners.

Furthermore, a purchaser for the oil/soot mixture is required which can be a disadvantage since the gasification process cannot be operated independently of the further processing and in addition the required oil must, for reasons of environmental protection, generally contain less sulphur than the oil used in the gasification.

However, in addition technical difficulties in the gasification occur if oil with a total level of more than about 100 ppm nickel and vanadium are to be gasified, if the soot produced is recirculated to the gasification reactor, and the sensible heat of the crude unpurified gas is intended to be used to produce high pressure steam.

The gasification process of the preceding paragraph is particularly important in the production of water gas for synthesis purposes, for combustion gas production, and reduction gas generation.

The effectiveness of the waste heat recovery plants, which are generally designed as fire tube boilers, is adversely affected by deposits of nickel sulphide and vanadium oxide, which are difficult to remove. The boilers eventually become blocked, with the result that costly purification operations combined with plant stoppages are necessary. For these reasons the gasification of high ash content and thus cheap fuel oils is at present largely avoided.

It is however expected that in the future there will be a scarcity in the supply of heavy, especially low ash fuel oil, as a result of the continuing processing of residue oils in conversion plants. Accordingly, the gasification of high ash content oils with substantial utilisation of the soot is necessary for gas generation. Furthermore the combustion of soot together with oil as a soot-oil mixture in power-stations may well be discontinued because at times there may be no need for steam and electricity, there may be restrictions on the sulphur content of the soot-oil mixture making the use of high quality oil necessary and oil may be considered too expensive compared with, e.g. coal, to be burnt.

An object of the invention is to provide a process for producing synthesis gas by gasification of hydrocarbons, the process enabling the use of high ash content hydrocarbons as feedstock in a largely self-sufficient gasification plant i.e. a power plant without auxiliary services e.g. from a power station burning the soot formed as a byproduct.

In accordance with the present invention, there is provided a process for producing synthesis gas by partial oxidation of one or more hydrocarbons containing nickel and vanadium in a concentration of 100 to 2000 ppm, with the formation of soot as a by-product, characterized in that the oxidation of the hydrocarbons to synthesis gas is carried out so that the soot is formed in a sufficient amount that the total concentration of nickel and vanadium in the soot does not exceed 5% by weight based on the soot, the synthesis gas is cooled to 160 to 350°C and the soot and ash are separated dry by means of one or more filters from the cooled synthesis gas.

The dry separated soot produced is suitable for further processing.

The process according to the invention uses one or more hydrocarbons as feedstock. Any suitable liquid hydrocarbons and hydrocarbon mixtures such as heavy fuel oil or residues from conversion plants may be used as the feedstock.

The partial combustion of the one or more hydrocarbons may be carried out according to any of the known prior art processes referred to above. A particular feature of the invention is the complete gasification of the feedstock oil without recirculating soot and thus ash, as was customary

hitherto. Mainly in this way, and assisted also by a somewhat increased soot production, effected in by controlling the supply of oxygen to the partial oxidation, the nickel and vanadium levels in the
 5 spot can be controlled at a maximum of 5%, a value at which no difficulties are caused by deposition in the fire tube boilers normally used for the gas cooling.

The soot-containing and ash-containing
 10 synthesis gas is cooled to temperatures of between 160 and 350°C. The cooling preferably takes place in waste heat boilers designed as fire tube boilers having relatively high flow rates (of 10—50 m/second) in order to avoid deposition of
 15 solids and thereby to avoid interference with the heat transfer.

The synthesis gas is then passed to one or more filters on which soot and ash are separated dry, i.e. without using water as an auxiliary phase.

20 The soot deposition may take place on commercially available filters. These filters are preferably used in a pressure resistant modification, but may otherwise be of conventional design, and are preferably flexible
 25 tube filters. Filters utilizing thermally stable fabric such as glass fibres or polytetrafluoroethylene as filter medium have proved particularly suitable. Filters with a pore diameter of 15 to 50 μ are advantageously used. The gas throughput per m²
 30 of filter surface should preferably be 100 to 350m³, and the pressure loss in the filter layer should preferably be 300 to 1000 pascals.

Soot and ash deposited on the filter are preferably periodically removed from the filter
 35 with recirculated pure gas. The soot recovered can be employed for various purposes, according to the desired end use. It has proved particularly suitable to convert the soot to synthesis gas in an auxiliary reactor, e.g. a chamber reactor or tubular
 40 reactor. Ash is formed in this reaction, the ash containing the total nickel and vanadium content of the original feedstock.

The soot can obviously also be used for some other purpose, e.g. can be removed by means of a
 45 hose system and used as a filler or can also be processed further into a fuel.

The invention is further described below by way of example with reference to the accompanying drawing, which shows
 50 diagrammatically apparatus suitable for use in carrying out the process according to the invention.

Referring to the drawings, heavy fuel oil, steam and oxygen or air are supplied through lines 1, 2
 55 and 3 respectively to a reactor 4 normally under elevated pressure, in which partial oxidation (i.e. gasification) of the fuel oil takes place.

The partial oxidation produces a gas mixture, which essentially consists of CO and H₂ and
 60 further contains methane, H₂S and COS as gaseous impurities and soot and ash as solids. The reaction conditions are such that the weight ratio (Ni+V)/C in the soot is not higher than 5%.

The gas mixture, including the solids contained
 65 therein, is supplied to a waste heat boiler 5 in order

to produce high pressure steam, which is withdrawn through a line 6. In the waste heat boiler 5 the gas is cooled to a temperature slightly above its saturated vapour pressure. The gas is
 70 then supplied to a feed water preheater 7 connected to the waste heat boiler 5. In the preheater 7 the gas is cooled to a temperature above its dew point (about 160°C) and below about 350°C, preferably 250°C. The temperature
 75 to which the gas is cooled in the preheater 7 is controlled by means of a temperature regulator 8 which can direct a controlled proportion of feed water to be supplied to the boiler 5 around the preheater.

80 The cooled gas is then led from the preheater 7 to at least one of several pressure resistant filter vessels 9, only one of which is shown in the drawing, each having a filter covered with a heat resistant fabric (e.g. glass fibres or

85 polytetrafluoroethylene fibres). The provision of several of the vessels connected in parallel enables continuous filtration to be achieved.

The soot is almost completely deposited as layers on the filter so that pure gas, i.e. gas free of
 90 solids, leaves the vessel 9. The filter of each vessel 9 is cleaned periodically by interrupting the supply of gas from the preheater 7 and recirculating pure gas. The soot layers removed fall discontinuously into a funnel-shaped lower
 95 part 10 of the filter vessel and are then collected as very voluminous ($\gamma \approx 150$ g/litre) pulverulent soot.

The pulverulent soot is stored in the lower part 10 of the filter vessel and is withdrawn
 100 continuously therefrom, the withdrawal of the soot being monitored by a level regulator 11.

The differential pressure required to withdraw the pulverent soot is produced by returning a proportion of the purified gas to the filter vessel 9
 105 upstream of the filters by means of a fan 20 and throttling the remaining proportion of the pure gas stream by means of a throttle 12 downstream of the filter vessel 9, in conjunction with the filter resistance.

110 During the cleaning of the filter in any of the filter vessels 9, the filtering of the soot from the synthesis gas supplied from the preheater 7 is carried out by the filter in one or more of the other filter vessels.

115 According to a preferred procedure, as shown in the drawing, the pulverulent soot together with the gas contained therein is withdrawn from the filter vessel and supplied to a small auxiliary reactor 13, in the form of, e.g. a chamber reactor
 120 or a tubular reactor. The soot is converted with oxygen and steam, which are supplied through a line 21, to form synthesis gas, in the auxiliary reactor 13. The synthesis gas is supplied together with liquid ash as a stream through a line 14 to a vessel 15 which is supplied with water through a
 125 line 16. The synthesis gas stream is quenched and washed with water in the vessel 15, and the liquid ash, which is present in only a small amount, is separated.

130 The ash, which is derived originally from the

oil, is removed from the vessel 15 as fine granules together with the water, either continuously or batchwise, through a hose system controlled by means of a regulating system 17, and is then
5 separated from the water by conventional separation equipment (e.g. settlers, filters). The resulting purified gas is removed through a line 18.

A proportion of the pure gas from the vessel 15 may be recycled to the filter 9 being cleaned
10 through a line 19 by means of the fan 20. During the cleaning of any of the filters 9, the filter being cleaned does not operate but is replaced by one of the filters connected in parallel as described above.

15 If it is intended to use the soot for purposes other than gasification it can be removed dry from the system by means of pressure locks.

Claims

1. A process for producing synthesis gas by
20 partial oxidation of one or more hydrocarbons containing nickel and vanadium in a concentration of 100 to 2000 ppm, with the formation of soot as a by-product characterized in that the oxidation of the hydrocarbons to
25 synthesis gas is carried out so that the soot is formed in a sufficient amount that the total concentration of nickel and vanadium in the soot does not exceed 5% by weight based on the soot, the synthesis gas is cooled to 160 to 350°C and
30 the soot and ash are separated dry by means of one or more filters from the cooled synthesis gas.

2. A process according to claim 1, wherein the one or more filters comprise glass fibre and/or polytetrafluoroethylene fabric as filter medium.

35 3. A process according to either preceding claim, wherein the one or more filters have a pore diameter of 15 to 50 μ .

4. A process according to any preceding claim, wherein the dry separated soot is converted in a
40 reactor, other than one used for the oxidation of the one or more hydrocarbons, into synthesis gas.

5. A process according to any preceding claim, wherein the soot and ash are not recycled to the oxidation of the one or more hydrocarbons.

45 6. A process according to any preceding claim, wherein the one or more hydrocarbons are ash rich.

7. A process according to any preceding claim, wherein the pressure loss of the synthesis gas in the one or more filters is 300 to 1000 pascals.

50 8. A process according to any preceding claim, wherein the rate of flow of the synthesis gas through the one or more filters is 100 to 350m³ per m² of filter surface.

55 9. A process according to any preceding claim, wherein the cooling of the synthesis gas is carried out in a fire tube boiler.

10. A process according to claim 9, wherein the flow rate of the synthesis gas through the fire
60 tube boiler is 10 to 50 m/sec.

11. A process according to claim 1, substantially as described herein with reference to the accompanying drawing.